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(54) Radiopaque, low visual opacity dental composites containing non-vitreous microparticles.

(57) Radiopaque, low visual opacity dental composites and non-vitreous microparticles for use therein, the microparticles individually containing amorphous silica microregions interpersed with radiopacifying polycrylstalline ceramic metal oxide microregions, the microparticles being substantially free of visually opacifying inclusions such as crystalline microregions having diameters greater than about 0.4 micrometers.

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RADIOPAQUE, LOW VISUAL OPACITY DENTAL COMPOSITES CONTAINING NON-VITREOUS MICROPARTICLES

Technical Field

This invention relates to composites containing
5 non-vitreous microparticles. In another aspect, it relates
to novel non-vitreous microparticles for use in such
composites, and to a process for making such composites.

Background Art

A variety of references have described
10 non-vitreous small particles, e.g., U.S. Patent Nos.
3,709,706, 3,793,041, 3,795,524, 4,166,147, 4,217,264, and
4,306,913 and U.K. published patent application no.
2115799. Some of the small particles described in such
references are combined with binders (e.g., polymerizable
15 resins) to form composites, and a few of such small
particles may contain sufficient amounts of a suitable
ceramic metal oxide to render composites which might be
made with such particles opaque to X-ray radiation (i.e.,
radiopaque).

20 Radiopacity is a very desirable property for
dental composites. Radiopaque composites can be examined
using standard dental X-ray equipment, thereby facilitating
long term detection of marginal leakage or caries in tooth
tissue adjacent to the cured composite. However, a dental
25 composite should also have low visual opacity, that is, it
should be substantially transparent or translucent to
visible light. Low visual opacity is desired so that the
cured dental composite will have a lifelike lustre. If
30 such a dental composite is intended to be cured or
polymerized using visible light-induced photoinitiation,
then the depth of cure required (sometimes as much as two
millimeters or more), the desire for uniform hardness in
the cured composite, and the physical limitations imposed
35 by carrying out the curing reaction within the mouth (which
require, among other things, that the uncured composite

usually be exposed to light from only one angle, and that the curing radiation be provided by a portable instrument) all mandate that the composite have low visual opacity to enable deep, thorough cure.

5   An additional desirable property for dental composites is durability. Durability sometimes can be improved by increasing the percentage of filler particles in the composite. However, increased filler levels typically lead to increased visual opacity, thus reducing

10 translucency and limiting visible-light cure depth and cure uniformity.

      A further desirable property for dental composites is cure stability. For a two-part non-light cure dental composite (i.e., a so-called "chemical cure"

15 composite), cure stability is evaluated by comparing polymerization set times for aged and unaged composite samples when the two parts of the composite are mixed together. For a one-part light-cure dental composite, cure stability is evaluated by comparing top and bottom

20 hardnesses of composite samples that have been aged or are unaged and are cured to a standard depth. Poor cure stability is manifested by a change in polymerization set time or a difference in top and bottom cure hardness between aged and unaged composite samples. The filler

25 particles in a dental composite sometimes interact with the other ingredients of the composite (e.g., with the polymerizable resin or the polymerization initiators) and adversely affect cure stability. These interactions can be unpredictable and are sometimes poorly understood.

30   In practice, it has proven very difficult to formulate dental composites having a commercially useful combination of high radiopacity, low visual opacity, high filler loading, and cure stability.

35   <u>Summary of the Invention</u>

      The present invention provides, in one aspect, a radiopaque dental composite, comprising a mixture of

(a) polymerizable resin suitable for use in the oral
environment, and (b) non-vitreous microparticles,
characterized in that said microparticles individually
comprise:

5   (i) a plurality of amorphous microregions
comprising oxide of silicon, substantially uniformly
interspersed with

           (ii) a plurality of crystalline microregions
comprising radiopacifying polycrystalline ceramic
10   metal oxide, and
said microparticles are substantially free of visually
opacifying inclusions.

In addition, the present invention provides novel
microparticles useful in such composites, and a process for
15 making such composites.

Other workers interested in making small parti-
cles for use in dental composites, e.g., those described in
said U.S. Patent Nos. 4,217,264 and 4,306,913, and said
U.K. published patent application no. 2115799 have
20 apparently sought to make such particles entirely amorphous
in order to provide a good refractive index match between
the small particle and the resin. The metal oxides used in
such small particles typically have refractive indices
greater than two, a value which greatly exceeds the refrac-
25 tive indices of conventional resins. In contrast to the
approach of such other workers, the present invention
provides microparticles which deliberately contain both
amorphous and crystalline microregions. Dental composites
having low visual opacity are obtained by ensuring that the
30 microparticles are substantially free of visually
opacifying inclusions. In a preferred embodiment, substan-
tially all of the crystalline microregions of such micropar-
ticles have diameters less than about 0.4 micrometers.

35   Brief Description of the Drawing
The accompanying drawing is a transmission
electron micrograph of an $SiO_2:ZrO_2$ microparticle (prepared

Detailed Description of the Invention

The term "radiopaque", when used to describe the dental composites of the present invention, refers to a cured composite exhibiting sufficient opacity to
5 X-radiation to enable the composite to be distinguished from tooth structure using standard dental X-ray equipment. The desired degree of radiopacity will vary depending upon the particular application and the expectations of the practitioner evaluating the X-ray film. A preferred degree
10 of radiopacity can be measured using the following test. A conventional dental X-ray film is exposed through a one mm thick cured layer of composite using a conventional radiation time and intensity. The X-ray negative is developed and its density evaluated using a Macbeth Transmission
15 Densitometer, Model TD 504, equipped with a visible light filter. Preferably, the indicated densitometer reading will be about 1.4 or less, more preferably 0.8 or less.

A "dental composite", as used herein, refers to a hardenable (or hardened) composition containing polymeriz-
20 able (or polymerized) resin(s), filler particles of one or more types, and any desired adjuvants, the resulting composite being suitable for use in the mouth. Dental composites of the present invention can be multiple part
25 chemical cure or one part UV- or visible-light cure compositions. The dental composites of the present invention find particular use as anterior or posterior restoratives, cavity liners, orthodontic bracket adhesives,
30 crown and bridge cements, artificial crowns and casting resins.

Polymerizable resins suitable for use in the dental composites of the present invention are hardenable organic resins having sufficient strength, hydrolytic
35 stability, and non-toxicity to render them suitable for use in the oral environment. Examples of such resins include acrylate, methacrylate, urethane, and epoxy resins, e.g., those shown in U.S. Patent Nos. 3,066,112, 3,539,533, 3,629,187, 3,709,866, 3,751,399, 3,766,132, 3,860,556,

4,002,669, 4,115,346, 4,259,117, 4,292,029, 4,208,190,
4,327,014, 4,379,695, 4,387,240 and 4,404,150, and mixtures
and derivatives thereof. A preferred polymerizable resin
for use in the present invention is a mixture of

5   diglycidylmethacrylate of Bisphenol A (frequently referred
to as "BIS-GMA") and triethyleneglycol dimethacrylate
(frequently referred to as "TEGDMA").

A "non-vitreous" microparticle, as used herein,
is a small diameter particle (preferably having a diameter

10 less than about 50 micrometers) which has not been derived
from a melt. A "microregion" is a portion of the
microparticle which when observed using transmission
electron microscopy at a magnification of about 100,000 to
1,000,000 appears uniformly shaded (or generally uniformly

15 shaded) and appears to contain a single crystalline or
amorphous inorganic species. The microparticles of the
invention can be characterized by the presence of a
plurality (i.e., two or more) of at least two distinctly
different types of microregions within individual

20 microparticles when so observed. The two types of
microregions are referred to herein as "amorphous micro-
regions" and "crystalline microregions". The amorphous
microregions are substantially uniformly interdispersed
with the crystalline microregions; that is, the amorphous

25 and crystalline microregions are substantially randomly
arrayed throughout individual microparticles. In order to
examine individual microparticles, a representative sample
(e.g., 10-100) of the microparticles should be studied, and
sintering bonds which may agglomerate individual micro-

30 particles together should be fractured, e.g., by mild
pulverization.

The presence of amorphous and crystalline micro-
regions in the microparticles can be further determined
using X-ray or electron diffraction or other techniques

35 suitable for examination of small amorphous or crystalline
species. Crystalline microregions are those which, when
examined using X-ray or electron diffraction analysis,

exhibit a characteristic distinguishing pattern of diffraction lines. Amorphous microregions are those which, even when present in an array of such microregions and observed using X-ray or electron diffraction analysis, do

5 not exhibit distinguishable lines. Because the microparticles of this invention contain both amorphous and crystalline microregions, the microparticles as a whole will exhibit a diffraction pattern. The presence of amorphous microregions in the microparticles is ascertained

10 by the absence of the characteristic diffraction pattern for the chemical species making up the amorphous microregion. Preferably, the amorphous microregions have diameters less than about 0.1 micrometers, and more preferably have diameters of about 0.002 to 0.05

15 micrometers.

A "radiopacifying" metal oxide is an inorganic oxide which, when present in the microparticles of this invention, inhibits the transmission of X-ray radiation through the microparticles to a degree sufficient to render

20 usefully radiopaque a dental composite made therewith. A "polycrystalline" metal oxide has a sufficient number of like crystalline microregions such that the unit cell structures thereof can be discerned or identified by examining the microparticles using X-ray or electron

25 diffraction analysis. Typically, the crystalline microregions will represent about one-half volume percent or more (preferably five volume percent or more) of the total volume of the microparticle. The actual volume percent will depend upon the type and amount of metal oxide

30 employed. Preferably, the crystalline microregions have diameters less than about 0.05 micrometers, and more preferably have diameters of about 0.001 to 0.01 micrometers, as determined using X-ray or electron diffraction analysis.

35 A "ceramic" metal oxide is an inorganic oxide which, when in its pure form, can be fired or sintered into a rigid or self-supporting polycrystalline form that is

stable in a normal air environment, e.g., 23°C and 50
percent relative humidity. Suitable ceramic metal oxides
are non-toxic when incorporated into the microparticle and
are colorless or only weakly colored, e.g., BaO, Bi_2O_3,
5   CaO, Nb_2O_5, Sb_2O_5, SnO_2, Ta_2O_5, TiO_2, Y_2O_3, ZnO, ZrO_2, and
oxides of the lanthanide series (e.g., CeO_2, Ce_2O_3 and
La_2O_3), as well as mixtures and mixed oxides thereof.
Preferred ceramic metal oxides include HfO_2, La_2O_3, SrO,
ZrO_2, and mixtures thereof, with ZrO_2 being most preferred.
10 Characteristically, substantially all (e.g., 90 weight
percent or more) of the radiopacifying ceramic metal oxide
in the microparticle is present in its polycrystalline
form, and substantially none (e.g., 10 weight percent or
less) is present in an amorphous form.

15   A preferred method for preparing the micropar-
ticles of the present invention, referred to herein as a
"sol-gel" method, involves the combining of (1) an aqueous
or organic dispersion or sol of amorphous silica with (2)
an aqueous or organic dispersion, sol, or solution of the
20 desired radiopacifying ceramic metal oxide or a precursor
organic or inorganic compound which is calcinable to the
desired radiopacifying ceramic metal oxide. For brevity,
the aforementioned dispersion or sol of silica will be
sometimes referred to hereafter as the "silica starting
25 material", and the aforementioned dispersion, sol, or
solution of the radiopacifying ceramic metal oxide or
precursor compound will sometimes be referred to hereafter
as the "ceramic metal oxide starting material". The
mixture of silica starting material and ceramic metal oxide
30 starting material is dried to a solid, ground, fired, and
reground to form microparticles of the invention. The
microparticles can then be combined with an appropriate
resin to form a composite of the invention.

          Although either aqueous or organic silica starting
35 materials can be employed in the sol-gel method, aqueous
silica starting materials are preferred for reasons of
economy. Suitable aqueous silica starting materials

about 1 to 50 weight percent, more preferably 15 to 35
weight percent. Suitable organic silica starting materials
include organosols containing colloidal dispersions of
silica in organic solvents (preferably water-miscible polar

5   organic solvents) such as ethanol, normal or isopropyl
alcohol, ethylene glycol, dimethylformamide and the various
"Cellosolve" glycol ethers. The size of the colloidal
silica particles in the silica starting material can vary,
e.g., from 0.001 to 0.1 micrometers, preferably about 0.002

10   to 0.05 micrometers.

Preferred silica starting materials which can be
used in this invention include aquasols sold under the
trademark "Ludox" from E. I. DuPont de Nemours and Co.
Other useful silica starting materials include dispersions

15   or aquasols sold under the trademarks "Nalco", "Syton" and
"Nyacol". Additional suitable commercially available
silica starting materials are listed in said U.S. Patent
Nos. 3,709,706 and 3,793,041.

Preferably, the silica starting material is

20   filtered to remove extraneous solids, bacterial growth and
other impurities. More preferably, the silica starting
material is filtered through a microfine filter, as
described in more detail below. If desired, the silica can
be modified by addition of other inorganic compounds, for

25   example, those compounds (e.g., B_2O_3) which can form
amorphous microregions under the conditions used to prepare
the microparticles of the present invention. It should be
borne in mind that the addition of such inorganic compounds
may alter the refractive index of the final microparticles,

30   and may affect the visual opacity of a dental composite
prepared therewith.

Although either aqueous or organic ceramic metal
oxide starting materials can be employed in the sol-gel
method, aquasols are preferred for reasons of economy.

35   Suitable commercially available ceramic metal oxide
aquasols include CeO_2, Sb_2O_5, SnO_2, and ZrO_2 aquasols.
Commercial ZrO_2 aquasols typically contain a small amount

(e.g., 1 to 3 weight percent) of HfO_2 as a contaminant.
Suitable calcinable precursor compounds preferably are
carboxylates (e.g., acetates, formates, oxalates, lactates,
propylates, citrates, or acetylacetonates) or salts of

5   mineral acids (e.g., nitrates), selection of particular
precursor compounds being dictated by availability and ease
of handling. Use of precursor compounds which might form
precipitates or undesired crystalline microregions prior to
gellation, or form water- or acid-soluble compounds or

10   colored impurities in the microparticles, preferably should
be avoided. Representative precursor compounds useful in
the present invention include barium acetate, lanthanum
nitrate, strontium nitrate, tantalum nitrate, and zirconium
acetate.

15   Other metal oxides which may not themselves
provide sufficient radiopacity can, if desired, be included
in the microparticles of the present invention. Such other
metal oxides can be useful, for example, to adjust various
physical properties of the microparticles (e.g., refractive

20   index, hardness, density or porosity) or physical
properties of dental composites prepared therewith (e.g.,
viscosity before cure, or compressive strength, tensile
strength, or visual opacity after cure). Such other metal
oxides include Al_2O_3 and CaO. When the above-described

25   sol-gel method of preparation is employed, such other metal
oxides can be introduced into the final microparticles by
combining a dispersion or sol containing the desired other
metal oxide (or a suitable dispersion or sol containing a
precursor compound calcinable thereto) with the silica

30   starting material and ceramic metal oxide starting
material. If desired, such other metal oxides can be
introduced by using a silica sol containing silica
particles coated with such other metal oxide (e.g., "Nalco"
612 or 613 alumina-coated silica aquasols).

35   In a most preferred embodiment, the sol-gel
method is carried out as follows. First, an aquasol
containing colloidal silica is mixed with a rapidly stirred

sol or solution containing the desired radiopacifying
ceramic metal oxide (e.g., ZrO_2) or calcinable precursor
compound (e.g., zirconium acetate). For some starting
materials, reverse order of addition can lead to
5   non-uniform interspersal of the amorphous and crystalline
microregions in the final microparticle. The mixture
preferably should be sufficiently acidic to prevent
non-uniform gelation from occurring. For example, the pH
preferably is below about 4.5 for a silica:zirconium
10   acetate mixture. The mixture is then gelled, e.g. by
raising the pH, by dehydration (using, for example, a
"Rotovap" apparatus), or by heating the mixture at a
temperature below its boiling point. For example,
dehydration by heating below about 75°C can be used for a
15   silica:zirconium acetate mixture.

The gel may contain a significant portion of the
water or other solvents present in the starting materials.
The gel is heated at a temperature and pressure sufficient
to remove the water or solvents without causing boiling of
20   the gel, e.g., for 20-24 hours at 75°C and ambient
pressure, thereby yielding a dried or substantially dried
solid. Drying preferably is carried out in shallow pans.
The dried solid breaks up into small granules. The small
granules preferably are pulverized or comminuted to
25   facilitate removal of organic compounds. The granules are
then heated at a temperature and pressure sufficient to
remove substantially all such organic compounds, e.g., in
air at atmospheric pressure for 2-4 hours at 200-600°C,
preferably 300-600°C. Differential thermal analysis or
30   gravimetric analysis can be used to determine the extent of
organic compound removal. The resulting powder is very
friable and can be further pulverized.

The powder is next fired at a temperature and for
a time sufficient to convert the ceramic metal oxide or
35   precursor to polycrystalline ceramic metal oxide. The
firing time and temperature should not be excessive, as it
is desirable to retain oxide of silicon in its amorphous

state, prevent the growth or formation of crystalline microregions having diameters greater than about 0.4 micrometers, and densify the microparticles to reduce the incidence of voids. During the firing cycle, the microparticles will undergo significant changes in density, surface area, pore volume and pore size. Density tends to increase during firing, while surface area and pore volume tend to decrease. For example, in 5.5:1 mole ratio $SiO_2:ZrO_2$ microparticles, density reaches about 2.50 gm/cc after firing to about 1000°C. Surface area reaches a maximum after firing to 400°C (at a value of about 175-200 m^2/g as measured by the BET method), declines after firing to 950°C (to a value of about 50-75 m^2/g), then declines further after firing to 1000°C (to a value of about 4-6 m^2/g). Average pore volume reaches about 40% of the microparticles (as determined using the BET method) after firing at 400-700°C, then drops to substantially zero after firing to about 1000°C. For $SiO_2:ZrO_2$ microparticles, firing should be carried out to an extent sufficient to form polycrystalline zirconia (e.g., tetragonal ZrO_2), while avoiding formation of zircon ($ZrSiO_4$) or cristobalite (SiO_2) crystalline microregions. Firing temperatures between about 1000 and 1100°C are preferred.

The term "green state milling" will be used herein to describe milling of the microparticles before the ceramic metal oxide has been fired to its polycrystalline form. Use of green state milling has been found to be very beneficial in obtaining dental composites with good cure stability, particularly when both green state milling and optimization of firing temperatures is employed.

To predict cure stability for dental composites prepared from $SiO_2:ZrO_2$ microparticles, it has been found useful to evaluate the pH of the microparticles after firing by contacting an aqueous slurry of the micro-particles with alizarin indicator. $SiO_2:ZrO_2$ microparticles which cause the indicator to turn yellow (pH<6) tend to form dental composites with better cure

stability than $SiO_2:ZrO_2$ microparticles which cause the indicator to turn pink-red (pH>7). The aforementioned green state milling step has been found useful for making $SiO_2:ZrO_2$ microparticles which cause alizarin indicator to

5   turn yellow.

In addition to the factors already noted above, higher firing temperatures tend to increase the hardness of the microparticles and decrease water absorption. Higher firing temperatures typically also lead to faster polymeri-

10   zation set times for dental composites prepared from the fired microparticles.

Firing can be carried out, for example, in a muffle furnace, with the dried powder contained in a shallow layer (e.g., 25 mm deep) in a vitreous silica boat.

15   The fired product is then reground to provide micropar- ticles having the desired average particle diameter, e.g., less than 50 micrometers. Regrinding can be carried out using conventional equipment and preferably employs grinding media having the same refractive index as the

20   microparticles.

The relative molar ratio of oxide of silicon to ceramic metal oxide in the microparticles should be adjusted to provide the desired refractive index and degree of radiopacity. For the most preferred $SiO_2:ZrO_2$

25   microparticles, the molar ratio of SiO_2 to ZrO_2 desirably is about 2:1 or more, with values between about 3:1 and 9:1 being preferred, and values between about 5:1 and 7.5:1 being most preferred. For microparticles containing other silica:ceramic metal oxide mixtures, the ratio of silica to

30   ceramic metal oxide should be adjusted to provide the desired degree of radiopacity coincident with attainment of the desired refractive index and other desired physical properties in the microparticles and attainment of the desired visual opacity, durability, cure stability, and

35   other desired physical properties in dental composites prepared therewith.

The relative ratio of oxide of silicon to ceramic
metal oxide can also influence polymerization set time
rates for dental composites prepared therewith, with higher
oxide of silicon content typically leading to faster set

5   times.

It is particularly desirable to avoid formation
within the microparticles of crystalline microregions or
inhomogeneities (e.g., voids) having diameters greater than
about 0.4 micrometers, a dimension which corresponds to the

10 shortest wavelength of visible light. The presence in the
microparticles of such crystalline microregions or
inhomogeneities will undesirably increase the visual
opacity of a dental composite prepared therewith. Thus,
the microparticles of the present invention are formulated

15 under conditions that substantially discourage or prevent
the formation of such crystalline microregions and
inhomogeneities. For brevity, such crystalline
microregions and inhomogeneities will sometimes be referred
to hereafter as "visually opacifying inclusions".

20   Prevention of visually opacifying inclusions can
be achieved by filtering the silica starting material
and/or ceramic metal oxide starting material through a
microfine filter having a pore diameter less than 0.4
micrometers. A preferred filtration technique employs a

25 series of progressively finer "Ballston" filters with the
last filter in the series having a pore diameter less than
about 0.2 to 0.25 micrometers. During subsequent
processing, the gel formed by combination of the starting
materials should be kept free of contaminants. During

30 firing of the dried and ground solid obtained from the gel,
care should be taken to avoid firing temperatures and times
which might promote growth of crystalline microregions to
an extent sufficient to form visually opacifying
inclusions, or promote reaction between the various

35 inorganic species within the microparticles and formation
of new crystalline microregions containing visually
opacifying inclusions. In general, firing temperatures

above about 1100°C tend to promote formation of visually opacifying inclusions (usually as enlarged or new crystalline microregions, or as voids or cracks) and thus should be avoided.

5   When used in visible light-cure dental composites of the invention, the refractive index of the micropar-ticles preferably should be matched to the refractive index of the composite resin, e.g., within about plus or minus 0.05, more preferably within about plus or minus 0.005.

10 With currently used resins, the microparticles preferably have a refractive index less than 1.60. A preferred method for adjusting the refractive index of the microparticles is by altering the ratio of oxide of silicon to ceramic metal oxide. The microparticle refractive index can be

15 approximately predicted by interpolation based on a comparison of the relative volume percent of silica to ceramic metal oxide (or equivalent of ceramic metal oxide if a calcinable precursor compound is employed) in the starting mixtures. The microparticle refractive index will

20 vary approximately linearly, based on the above volume percent comparison, between the refractive index of pure amorphous SiO_2 (R.I. 1.459) and that of the ceramic metal oxide when in the polycrystalline form which it adopts within the microparticle.

25   It is desirable to avoid the incorporation of fluxes which may cause melting of the microparticles during firing and formation of vitreous inclusions. Also, the starting mixtures preferably are substantially free of chloride ion, as chloride ion may cause dental composites

30 containing the fired microparticles to exhibit undesirable discoloration as well as reduced shelf life.

When viewed without magnification or under optical magnification, the microparticles of the invention are a finely divided white or off-white powder having a

35 uniform appearance. Identification of the microstructure of such microparticles preferably is carried out using transmission electron microscopy ("TEM"). Scanning

electron microscopy ("SEM") typically does not reveal the
microstructure adequately, since under SEM the micro-
particles have a uniform greyish appearance. However,
under TEM the microparticle microstructure is very
5   distinctive and can be appreciated readily.

The drawing is a TEM image of a microparticle of
Example 1, at a magnification of 300,000X. The sample was
prepared by mixing the microparticles with aluminum powder,
compressing the mixture at a pressure of about 0.7 to 1.4
10   MPa, and heating the mixture to approximately 600°C to
embed the microparticles in an aluminum matrix. Slices
were cut from the matrix with a diamond saw and
mechanically polished to a thickness of approximately 200
micrometers. The slices were then ion beam milled (using a
15   "Gatan" dual ion mill apparatus) to render the slices
transparent to an electron beam. The ion beam milling was
carried out under an argon atmosphere and both sides of the
slice were milled simultaneously. During milling, the
slice was rotated constantly, the gun voltage was varied
20   from 7 KV to 4 KV, and the gun angle was varied from 15
degrees to 8 degrees. The milled slice was photographed
using a JEOL Model "100CX" transmission electron microscope
operated at an accelerating voltage of 100 KV.

Boundary 11 represents the outer edge of the
25   microparticle. Circular amorphous microregions 13 contain
amorphous SiO_2 and are generally uniformly shaded. The
very slightly mottled appearance of amorphous microregions
13 is visible under TEM in the original colloidal silica
aquasol particles from which the sample was prepared and
30   may be accentuated somewhat by transmission through
crystalline ZrO_2 microregions (not shown) within the
interior of the slice. Smaller crystalline microregions 15
are darker (greyer) in color than microregions 13, and
contain tetragonal ZrO_2. Amorphous microregions 13 are
35   substantially uniformly dispersed with crystalline
microregions 15. The microparticle appears fully dense and
shows no visually opacifying inclusions. The high

compressive strength of dental composites prepared
therewith is thought to be due, in part, to the many grain
boundaries within the microparticle. Such grain boundaries
exist between adjacent amorphous and crystalline microre-
gions, and between adjacent crystalline microregions, and
serve to blunt or discourage crack propagation through the
microparticle.

Typically, the dental composites of the present
invention will contain chemical polymerization initiation
systems such as peroxide compounds alone or in combination
with suitable amines, sulfur compounds, phosphorus
compounds or other chemical compounds capable of reacting
with the peroxide to generate free radical species.
Alternatively, the dental composites of the present
invention can contain light-induced polymerization
initiation systems such as ketone or alpha diketone
compounds alone or in combination with suitable amines,
peroxides, sulfur compounds, phosphorous compounds, or
other chemical compounds capable of reacting with or being
sensitized by the ketone or alpha-diketone compounds to
effect polymerization of the dental composite resin. The
dental composites of the present invention can also contain
suitable adjuvants such as accelerators, inhibitors,
stabilizers, pigments, dyes, viscosity modifiers, extending
or reinforcing fillers, surface tension depressants and
wetting aids, antioxidants, and other ingredients well
known to those skilled in the art.

The amounts and types of each ingredient in the
dental composite should be adjusted to provide the desired
physical and handling properties in the composite before
and after cure. For example, the cure rate, cure
stability, fluidity, compressive strength, tensile strength
and durability of the composite typically are adjusted by
altering the types and amounts of polymerization initiators
and the loading and size distribution of the microparticles.
Such adjustment typically is carried out empirically based
on experience with dental composites of the prior art. For

use as a casting resin, the dental composite typically will
contain 45 weight percent or more of the microparticles.
For other applications (e.g., anterior or posterior
restoratives, cavity liners, orthodontic bracket adhesives,
5 crown and bridge cements and artificial crowns) higher
microparticle loading levels typically will be employed. -
For maximum compressive strength (e.g., for posterior use),
it is preferred that the dental composite be a "resin
bonded ceramic" or "RBC". In an RBC composite, the volume
10 of resin should be less than the void volume that would be
found in a sample of the microparticles when such
microparticles are in a dry, dense state. An RBC composite
inherently will contain a small volume of air or other gas.
An RBC composite typically will contain at least 70 volume
15 percent or more of the microparticles, and up to 30 volume
percent of resin. An RBC composite will be stronger than a
composite (referred to herein as a "resin expanded"
composite) which has been filled with resin to an extent
sufficient to displace all voids in the composite, since in
20 a resin expanded composite the microparticles will tend to
be spaced apart rather than touching.

In a preferred embodiment, the dental composites
of the present invention contain submicron silica
particles, e.g., pyrogenic silicas such as the "Aerosil"
25 "OX 50", "130", "150" and "200" silicas sold by Degussa and
"Cab-O-Sil M5" silica sold by Cabot Corp. "Aerosil OX 50"
is a preferred submicron silica. The submicron silica
particles preferably are silane-treated to enhance wetting
thereof by the resin.
30 Dental composites containing specified amounts of
submicron silica particles and microparticles of the
present invention have especially desirable handling
properties in the uncured state and exceptionally high
compressive strength and diametral tensile strength in the
35 cured state. The following amounts of submicron silica
particles, microparticles, and resin are preferred:

Type of product	submicron silica, wt.%	microparticles, wt.%
casting resin	8-32	48-72
cavity base	< 10	60-80
orthodontic bracket adhesive	< 10	70-80
anterior restorative	2-16	64-78
posterior restorative or crown material	10-25	65-80

Optimization of compressive strength and diametral tensile strength in such products has been found to depend upon the amounts and surface areas of fillers in the composite. The following calculation is useful. In the calculation, the surface areas of the submicron silica particles and microparticles are measured before silane treatment and the indicated weight fractions are based on weights measured after silane treatment. The term "total filler" refers to the combined weight of the silane-treated submicron silica particles and silane-treated microparticles in the composite. In a first step, the surface area of the submicron silica particles is multiplied by the weight fraction of submicron silica particles in the total filler. In a second step, the surface area of the microparticles is multiplied by the weight fraction of microparticles in the total filler. The multiplication products from the first and second steps are then added together and multiplied by the weight fraction of total filler in the composite. The result, referred to herein as the "net surface area" of the composite, can be used to optimize compressive strength and diametral tensile strength independently of total filler loading. For example, for composites containing "Aerosil OX 50" submicron silica particles and $SiO_2:ZrO_2$ microparticles, compressive strength increases from a value of about 390 MPa at a net surface area of about 5 m^2/g, to a peak value of about 440-480 MPa at net surface areas of about 7 or more m^2/g; diametral tensile strength first

increases and then decreases as net surface area is increases, exhibiting a value above about 75 MPa at net surface areas of about 5-22 m^2/g, and a value above about 90 MPa at net surface areas of about 7-15 m^2/g.

5   The dental composites of the present invention can be packaged and dispensed using means well known to those skilled in the art, e.g., multiple-part or one-part packages contained in jars, tubes, amalgamator capsules, syringes, and the like.

10   In addition to their use in dental composites, the microparticles of the present invention can be used in plastic composites intended for non-dental uses. Suitable resins for use in such composites include the resins already mentioned above, as well as thermosetting or

15   thermoplastic resins such as polyester resins, acetyl resins, amino resins (e.g., urea-formaldehyde and melamine formaldehyde resins), alkyd resins, cellulosic resins (e.g., ethyl cellulose, cellulose acetate, and cellulose propionate resins), fluorocarbon resins, furane resins,

20   polyurethane resins, phenolic resins, polyamide resins, polycarbamate resins, vinyl aromatic resins (e.g., styrene), polyolefin resins (e.g., polyethylene), and the like.

        Plastic composites of the present invention can

25   contain other adjuvants such as polymerization initiators, accelerators, inhibitors, stabilizers, pigments, dyes, viscosity modifiers, extending or reinforcing fillers, surface tension depressants and wetting aids, antioxidants, and other ingredients well known to those skilled in the

30   art.

        The microparticles of the present invention can also be used as a reinforcement agent in metal matrix composites or ceramic composites, or as abrasion resistant and/or reinforcing agents for elastomeric materials of the

35   types described in said U.S. Patent Nos. 3,709,706 and 3,793,041.

The following examples are offered to aid
understanding of the present invention and are not to be
construed as limiting the scope thereof.

Example 1

5   1,065.6 grams of a 31 weight percent colloidal
silica aquasol ("Ludox LS", commercially available from
E. I. du Pont De Nemours & Co.) was acidified by the
addition of 11 grams of concentrated nitric acid, diluted
1:1 with deionized water, and filtered through 2 microfine

10   filters placed in series. The first microfine filter was a
"Ballston grade B" filter having a pore diameter of 2 micro-
meters, and the second microfine filter was a "Ballston
grade AA" filter having a pore diameter of 0.25 micro-
meters. 492.8 Grams of aqueous zirconyl acetate (containing

15   25 weight percent equivalent ZrO_2) was similarly diluted
and filtered. The aqueous zirconyl acetate was placed in a
glass beaker and stirred with a nylon blade mounted on a
glass rod and rotated by an air stirrer motor. The
colloidal silica aquasol was poured slowly into the vortex

20   formed in the stirred aqueous zirconyl acetate, to provide
a mixture containing an equivalent $SiO_2:ZrO_2$ molar ratio of
5.5:1. The resulting mixture was stirred for 15 minutes,
then poured into "Pyrex" glass rectangular cake pans to a
depth of about 25 millimeters. The pans were placed in a

25   75°C forced air oven for 24 hours, then removed for
inspection. A loose granular powder, bluish-white in
appearance, had formed in the bottom of the pans. The pans
were placed in a 280°C forced air oven for 24 hours, then
removed and allowed to cool to room temperature. A weakly

30   agglomerated powder, white in appearance, was removed from
the pans and ball milled for a total milling time of 60
minutes in a ceramic mill jar containing 12 millimeter
diameter by 12 millimeter long ceramic rod media.
Subsequent measurements indicated that the grinding

35   distribution obtained after 60 minutes could have been
acheived with only 45 minutes of milling time. The milled

powder was placed in rectangular vitreous silica saggers at a depth of about 19 millimeters and heated in a muffle furnace for 16 hours at 400°C. The temperature of the muffle furnace was then raised 100°C every half hour.

5 Following one half hour at 900°C, the temperature of the muffle furnace was raised to 950°C for one hour and 1000°C for three hours. The saggers were removed from the muffle furnace and allowed to cool in air. The resulting fired powder was weakly agglomerated and white in appearance. It

10 was milled for 15 minutes in the ceramic ball mill described above. Subsequent measurements indicated that the grinding distribution obtained after 15 minutes could have been achieved with 5 to 10 minutes of milling time. The milled microparticles had a maximum diameter of 30

15 micrometers and a mean diameter of 4.5 micrometers. About 16 weight percent of the microparticles had diameters less than one micrometer. Weight loss measurements indicated no attrition of the mill liner or milling media occurred, thus indicating that the microparticles could be readily

20 fractured using low energy input.

The microparticles were silane-treated by slurrying 100 grams of the microparticles with 200 milliliters of cyclohexane for 30 minutes. A mixture of five grams of gamma-methacryloxypropyl trimethoxysilane

25 (commercially available from Union Carbide Corp.) and two grams n-propyl amine was added to the slurry. Mixing was allowed to continue for one hour. The slurry was then dried overnight in a fume hood followed by further drying in a forced air oven at 41°C for one hour and at 105°C for two

30 hours.

A visible-light cure dental composite having especially useful performance as a posterior restorative was prepared from the silane-treated microparticles by thoroughly mixing the following ingredients:

35

Ingredient	Amount, weight percent
BIS-GMA	9.5
Triethyleneglycol dimethacrylate	9.5
Silane-treated microparticles	80.0
Camphoroquinone	0.5
Dimethylaminophenethanol	0.5
	100.0

A sample of the resulting composite was placed in a 4.06 mm
I.D. glass tube capped with silicone plugs in each end of
the tube. The tube was placed in a test rig pressurized
with air at 0.28 MPa. The test rig contained two Espe
"Elipar" dental curing lights aimed at opposing sides of
the tube and mounted on a turntable which enabled the
lights to be rotated around the tube in a 180° arc. The
light guide of each curing light was spaced 3 mm from the
tube wall. While operating both curing lights
simultaneously and oscillating them continuously around the
tube, the tube was exposed to four 20 second curing cycles
from the curing lights. The tube was removed from the test
rig, placed on a pair of spaced rollers, and rotated under
a 110 watt "Ritter" dental operatory light at a distance of
0.6 meters for one hour. The cured sample was removed from
the tube and sliced into cylinders with a diamond saw. For
compressive strength testing, an 8.23 mm long cylinder was
employed, and for diametral tensile strength testing a
2.21 mm long cylinder was employed. The cylinders were
stored in 37°C distilled water for 24 hours, then tested
according to ADA Specification Nos. 8 and 27. The
compressive strength of cured samples of the composite was
394 MPa (4,016 kilograms/cm^2) and the diametral tensile
strength was 80 MPa (316 kilograms/cm^2).

Disc-shaped one millimeter thick by 20 millimeter
diameter samples of the composite were cured by exposing
them to illumination from an Espe "Elipar" dental curing
light for 60 seconds on each side of the disk at a distance

of 6 millimeters. The cured composite samples were then evaluated for visual opacity and radiopacity as follows.

Cured composite samples were measured for direct light transmission by measuring transmission of light through the thickness of the disk using a MacBeth transmission densitometer Model TD-504 equipped with a visible light filter. The densitometer value of 0.30 thereby obtained was assigned to the composite sample as its visual opacity value. Under visual examination, the cured composite samples had a greater translucency than tooth structure of comparable thickness, and readily could be pigmented to match natural dentition.

Cured composite samples were exposed to X-radiation using a Siemens "Heliodent" dental X-ray unit for 0.25 seconds at 7 milliamps and 50 kV peak voltage at a distance of about 250 millimeters. The X-ray negative was developed using a Litton "Profexray" automatic film processor. Using the Macbeth Transmission densitometer, a film density value of 1.25 to 1.30 was obtained and was assigned to the composite sample as its radiopacity value. When emplaced in a tooth and examined by X-ray, the composite readily could be distinguished from adjacent tooth structure.

Additional samples of the composite were cured in a 6 millimeter diameter by 2.5 millimeter deep cylindrical mold by exposing the samples to illumination from an Espe "Elipar" dental curing light for 20 seconds at a distance of zero millimeters. Barcol hardness testing of the top ard bottom surfaces of the thus-cured samples using indenter number 934-1 (commercially available from the Barber Colman Co.) yielded average top and bottom hardness values of 81 and 80 respectively.

Repetition of the above example using starting materials that were unfiltered or filtered through filters with a pore diameter greater than 0.4 micrometers (e.g., a filter with a pore diameter of two micrometers) provided dental composites with a visual opacity of about 0.40 to

0.41. The cured composite samples had a more opaque
appearance than tooth structure of comparable thickness.
Addition of pigments to match tooth coloration typically
would raise the visual opacity further, by about 0.01 to
5   0.02 visual opacity units, and would make the resulting
composites noticeably more opaque than tooth structure of
comparable thickness. Barcol top and bottom hardness values
averaged 80 and 75, respectively, indicating that the
degree of cure for such composites was less than that
10 obtained using the filtered sol dental composite described
above.

                        Examples 2-14
        Using the method of Example 1, a variety of
microparticles were prepared from unfiltered sols,
15 · formulated into two-paste chemical cure dental composites,
and evaluated for visual opacity and radiopacity. The
dental composites contained 70-76 weight percent micropar-
ticles, so the observed visual opacity values were in many
cases lower than the value of 0.30 obtained in Example 1,
20 and the observed radiopacity values numerically higher
(i.e., less radiopaque) than the value of 1.25 to 1.30
obtained in Example 1. Set out below in Table I are the
Example No., ceramic metal oxide exmployed, silica:ceramic
metal oxide mole ratio, microparticle refractive index,
25 microparticle-resin refractive index difference, visual
opacity and set time for composites prepared from micro-
particles fired at 900°C, 950°C or 1000°C, and radiopacity
for dental composites prepared from microparticles fired at
1000°C.
30   Repetition of these examples using filtered sols
would provide comparable or identical microparticle
refractive index values, microparticle-resin refractive
index difference values, and set time and radiopacity
values. Visual opacity values would be lower.
35

Table I

| | | | | Visual opacity[1] | | | Two paste chemical cure set time, min/sec | | | Radiopacity[1] |
Ceramic metal oxide	SiO₂:ceramic metal oxide mole ratio	Microparticle refractive index	Microparticle-resin refractive index difference	900°C	950°C	1000°C	900°C	950°C	1000°C	1000°C
ZrO₂	2:1	1.564	0.024	0.49	0.50	0.56	8'	6'	2'45"	0.71
ZrO₂	3:1	1.560	0.020	0.44	0.44	0.44	8'	6'	2'30"	0.84
ZrO₂	4:1	1.556	0.016	0.31	0.32	0.33	8'	6'	2'30"	0.96
ZrO₂	5:1	1.546	0.006	0.13	0.22	0.23	6'	5'30"	2'30"	1.11
ZrO₂	5.5:1	1.544	0.004	0.13	0.13	0.19	5'	3'30"	2'20"	1.21
ZrO₂	6:1	1.542	0.002	0.14	0.15	0.18	4'45"	3'15"	2'10"	1.29
ZrO₂	6.5:1	1.537	0.003	0.14	0.16	0.19	4'30"	3'15"	2'00"	1.34
ZrO₂	7:1	1.531	0.009	0.17	0.20	0.26	4'15"	3'10"	2'00"	1.35
ZrO₂	7.5:1	1.531	0.009	0.18	0.20	0.28	3'40"	3'10"	1'50"	1.40
ZrO₂	8:1	1.529	0.011	0.21	0.24	0.28	3'35"	3'05"	1'50"	1.40
ZrO₂	9:1	1.525	0.15	0.23	0.30	0.34	3'30"	3'00"	1'50"	1.41
ZrO₂+SrO	7.2:1[2]	1.524-28	0.016-12	0.26[4]	0.33	>0.50	—	1'45"	—	—
ZrO₂+BaO	8.5:1[3]	1.530	0.010	0.26[4]	0.36	0.36	—	1'50"	—	—

Examples 13 and 14 had 76.6 and 76 weight percent microparticle loadings, respectively. All other Examples had 70 weight percent microparticle loadings.

Based on total ceramic metal oxide. Microparticles contained SiO₂:ZrO₂:SrO in a 21.8:2:1 ratio. A strontium acetate solution containing 25wt% equivalent SrO was employed as the source of SrO.

Based on total ceramic metal oxide. Microparticles contained SiO₂:ZrO₂:BaO in a 25.8:2:1 ratio. A 25wt% barium acetate solution was employed as the source of BaO.

Greenish coloration.

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Examples 15-41

Using the method of Example 1, a variety of microparticles were prepared from filtered sols, formulated into two-paste chemical cure dental composites, and

5   evaluated for visual opacity and radiopacity. The dental composites contained 40-80 weight percent microparticles, and 0-40 weight percent silane-treated "Aerosil OX 50" pyrogenic submicron silica particles. Set out below in Table II are the Example No., ceramic metal oxide employed,

10   silica:ceramic metal oxide mole ratio, and the weight percent microparticles, weight percent submicron silica particles, visual opacity, compressive strength, diametral tensile strength, radiopacity, and top and bottom Barcol hardness values for the resulting composites.

TABLE II

Ex. No.	Ceramic metal oxide	SiO₂:ceramic metal oxide mole ratio	Weight % micro-particles	Weight % submicron silica	Visual opacity	Compressive strength, MPa (Kg/cm²)	Diametral tensile strength, MPa (Kg/cm²)	Radiopacity	Barcol hardness top/bottom
5	ZrO₂	2:1	80	0	0.59	349(3559)	71(720)	0.83	—
6	ZrO₂	2:1	76	4	0.61	366(3729)	51(519)	0.88	—
7	ZrO₂	2:1	40	40	0.67	374(3813)	49(497)	1.69	—
8	ZrO₂	3:1	78.4	0	0.42	356(3635)	73(746)	1.23	—
9	ZrO₂	3:1	76	4	0.44	371(3783)	81(823)	1.28	—
0	ZrO₂	3:1	40	40	0.52	360(3666)	46(465)	1.94	—
1	ZrO₂	9:1	76	0	0.36	333(3401)	71(724)	2.00	—
2	ZrO₂	9:1	76	4	0.33	354(3606)	76(778)	1.99	—
3	ZrO₂	9:1	40	40	0.29	391(3984)	82(832)	2.09	—
4	HfO₂	2:1	80	0	0.76	196(2000)	26(267)	0.50	67/52
5	HfO₂	2:1	76	4	0.62	221(2252)	36(371)	1.58	74/45
6	HfO₂	2:1	40	40	0.60	359(3659)	50(514)	0.63	68/60
7	HfO₂	9:1	78	0	0.44	294(2993)	54(548)	1.63	80/79
8	HfO₂	9:1	76	4	0.44	313(3195)	58(592)	1.71	80/80
9	HfO₂	9:1	40	40	0.42	367(3744)	67(681)	2.15	78/75
0	La₂O₃	2:1	75	0	0.79	268(2729)	34(352)	1.97	72/0
1	La₂O₃	2:1	76	4	0.79	330(3366)	37(380)	2.01	70/10

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TABLE II (cont.)

Ceramic metal oxide	SiO$_2$:ceramic metal oxide mole ratio	Weight % micro-particles	Weight % submicron silica	Visual opacity	Compressive strength, MPa (Kg/cm^2)	Diametral tensile strength, MPa (Kg/cm^2)	Radiopacity	Barcol hardness top/bottom
La$_2$O$_3$	2:1	40	40	0.70	381(3888)	26(261)	2.28	78/30
La$_2$O$_3$	9:1	78	0	0.47	260(2654)	55(560)	1.78	78/70
La$_2$O$_3$	9:1	76	4	0.52	277(2825)	60(614)	1.85	74/65
La$_2$O$_3$	9:1	40	40	0.48	366(3733)	62(635)	2.20	74/66
SrO	2:1	75	0	0.67	303(3094)	52(527)	1.47	68/28
SrO	2:1	76	4	0.68	315(3213)	37(374)	2.72	80/25
SrO	2:1	40	40	0.59	360(3670)	66(676)	2.00	85/74
SrO	9:1	62.3	0	0.98	259(2637)	34(349)	2.32	71/60
SrO	9:1	76	4	1.45	35(356)	1(13)	2.28	0/0
SrO	9:1	40	40	0.76	252(2566)	27(272)	2.37	78/67

* At 76 weight percent microparticles, this composite did not form a smooth paste, but instead formed a wet powder. Low strength and hardness values were obtained. Somewhat lower loading levels would yield higher strength and hardness values.

Example 42
Casting Resins

Varying amounts of the microparticles of
Example 1 were combined with varying amounts of
5 silane-treated "Aerosil OX 50" pyrogenic silica particles
and a sufficient quantity of the resin of Example 1 to form
composites containing 80 weight percent total filler (based
on the combined weight of fillers after silane treatment)
and 20 weight percent resin. The microparticles had a
10 surface area (before silane treatment) of 5 m^2/g, and the
pyrogenic silica particles had a surface area (before
silane treatment) of 41 m^2/g. Set out below in Table III
are the volume percent and weight percent of submicron
silica particles, microparticles, and resin for the
15 resulting composites, together with their compressive
strength, diametral tensile strength, and visual opacity.

Table III

Submicron silica		Microparticles		Resin		Compressive strength, MPa	Diametral tensile strength, MPa	Visual opacity
Vol.%	Wt.%	Vol.%	Wt.%	Vol.%	Wt.%			
1.81	2	62.04	78	36 15	20	396	78	0.34
2.52	2.8	61.36	77.2	36.12	20	402	79	0.36
3.61	4	60.32	76	36.07	20	400	84	0.37
7.19	8	56.89	72	35.91	20	428	86	0.38
0.72	12	53.5	68	35.77	20	446	91	0.39
4.24	16	50.15	64	35.61	20	445	93	0.39
7.73	20	46.81	60	35.46	20	445	91	0.40
1.19	24	43.5	56	35.31	20	451	95	0.39
3.02	32	36.97	48	35.01	20	456	92	0.41
4.72	40	30.56	40	34.72	20	463	87	0.41
1.33	48	24.24	32	34.43	20	477	88	0.41

Composites containing 4-40 weight percent submicron silica
were pourable syrups in which bubbles rose to the surface,
indicative of unusually low viscosity. Only a few
commercially available dental composites contain 80 or more
5 weight percent filler, and those that do are stiff, barely
stirable pastes.

Example 43

High Strength Posterior Composites

Varying amounts of the microparticles, submicron
10 silica particles, and resin of Example 42 were combined to
form RBC composites containing up to 90 weight percent
total filler (based on the combined weight of fillers after
silane treatment). Set out below in Table IV are the
volume percent and weight percent of submicron silica
15 particles, microparticles, total filler, and resin for the
resulting composites, together with their compressive
strength, diametral tensile strength, and visual opacity.
The composite containing 90 weight percent filler had a net
surface area of
20 $[(41 \text{ m}^2/\text{g})(0.18/0.9) + (5 \text{ m}^2/\text{g})(0.72/0.9)](0.9) = 11.2 \text{ m}^2/\text{g}$

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Table IV

micron silica		Microparticles		Total filler		Resin		Compressive strength, MPa	Diametral tensile strength, MPa	Visual opacity
.%	Wt.%	Vol.%	Wt.%	Vol.%	Wt.%	Vol.%	Wt.%			
34	8.67	66.07	78.03	74.4	86.7	25.59	13.3	446	93	0.39
82	13.2	63.9	74.8	76.7	88	23.28	12	444	94	0.42
73	18.0	62.5	72.0	80.3	90	19.73	10	483	97	0.44
09	21.97	55.68	65.93	76.8	87.9	23.23	12.1	473	97	0.42

These composites exhibited outstanding strength values and excellent handling properties. The composite containing 90 weight percent total filler was sent to the Forsyth Dental Center in Boston, Massachusetts and placed in molars of

5   Mucacca Fasicularis monkeys for an extended clinical study. After six months, the composite exhibited no visually detectable wear. The composite had a very desirable consistency in its uncured state. It could be tamped into a prepared tooth without excessive sticking or rebounding,

10 and in the view of the consultant supervising the clinical study, it handled "more like amalgam" than any plastic composite he had ever encountered. An amalgam-like consistency is especially desirable si..ce dentists have had extensive training and experience placing amalgam

15 restorations in posterior teeth.

Various modifications and alterations will be apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited

20 to the illustrative embodiments set forth herein.

CLAIMS:

1. Radiopaque dental composite, comprising a mixture of (a) polymerizable resin suitable for use in the oral environment, and (b) non-vitreous microparticles, characterized in that said microparticles individually comprise:

(i) a plurality of amorphous microregions comprising oxide of silicon, substantially uniformly interspersed with

(ii) a plurality of crystalline microregions comprising radiopacifying polycrystalline ceramic metal oxide, and

said microparticles are substantially free of visually opacifying inclusions.

2. Composite according to Claim 1, further characterized in that said amorphous microregions have diameters of 0.002 to 0.05 micrometers, said crystalline microregions have diameters of 0.001 to 0.01 micrometers, 90 weight percent or more of said radiopacifying ceramic metal oxide in said microparticles is present in its polycryst. lline form, said microparticles are substantially free of crystalline microregions having diameters greater than 0.4 micrometers, and wherein said composite, if prepared with an 80 weight percent loading of said microparticles, exhibits a radiopacity less than or equal to 1.4 and a visual opacity less than 0.40.

3. Composite according to Claim 1 or Claim 2, further characterized in that said ceramic metal oxide is selected from the group consisting of HfO_2, La_2O_3, SrO, ZrO_2, and mixtures thereof.

4. Composite according to any preceeding claim, further characterized by comprising a one-part visible light-cure resin bonded ceramic containing a mixture of:

    (a) up to 30 volume percent of said polymerizable resin, and

    (b) at least 70 volume percent of said non-vitreous microparticles,

wherein said oxide of silicon comprises silica, said ceramic metal oxide comprises tetragonal zirconia, the molar ratio of said silica to said zirconia is between 2:1 and 9:1, and said microparticles have diameters less than 50 micrometers and an index of refraction less than 1.60.

5. Composite according to any preceeding claim, further characterized by containing submicron silica particles, said composite having a net surface area of 5 to 22 m^2/g.

6. Composite according to Claim 5, further characterized by containing 10 to 25 weight percent of said submicron silica particles, 65 to 80 weight percent of said microparticles, and having a net surface area of 7 to 15 m^2/g, a compressive strength of at least 440 MPa, and a diametral tensile strength of at least 90 MPa.

7. Non-vitreous microparticles for use in a composite according to claim 1, characterized by having a diameter less than about 50 micrometers and individually comprising:

    (a) a plurality of amorphous microregions comprising oxide of silicon, substantially uniformly interspersed with

    (b) a plurality of crystalline microregions comprising radiopacifying polycrystalline ceramic metal oxide,

said microparticles being substantially free of visually opacifying inclusions.

8. Microparticles according to Claim 7, further characterized in that said oxide of silicon comprises silica, said ceramic metal oxide comprises tetragonal zirconia, the molar ratio of said silica to said zirconia is between 2:1 and 9:1, and said microparticles have an index of refraction less than 1.60 and are substantially free of crystalline microregions having diameters greater than 0.4 micrometers.

9. A process for making a radiopaque dental composite, characterized by the steps of:

(a) filtering an aqueous or organic dispersion or sol of amorphous silica through a microfine filter having a pore diameter less than 0.4 micrometers;

(b) filtering an aqueous or organic dispersion, sol, or solution of radiopacifying ceramic metal oxide, or a precursor organic or inorganic compound which is calcinable thereto, through a microfine filter having a pore diameter less than 0.4 micrometers;

(c) combining and gelling the filtered products of steps (a) and (b);

(d) heating the resulting gelled product at a temperature and pressure sufficient to remove the water or solvents therefrom without causing boiling thereof, to form a green state powder;

(e) milling said green state powder to reduce the particle size thereof;

(f) firing the resulting milled powder to convert said ceramic metal oxide or precursor compound to polycrystalline ceramic metal oxide, while preventing the growth or formation of crystalline microregions having diameters greater than 0.4 micrometers;

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    (g)   milling the resulting fired powder to form
          microparticles which individually comprise

          (i)   a plurality of amorphous microregions
               comprising oxide of silicon, substan-
               tially uniformly interspersed with

          (ii) a plurality of crystalline microregions
               comprising radiopacifying
               polycrystalline ceramic metal oxide;

    (h)   silane-treating said microparticles to
          facilitate wetting thereof by polymerizable
          resin; and

    (i)   mixing the resulting silane-treated
          microparticles with polymerizable resin
          suitable for use in the oral environment to
          form said composite.

      10. A process according to Claim 9, further
characterized in that said polycrystalline ceramic metal
oxide is selected from the group consisting of HfO_2, La_2O_3,
SrO, ZrO_2, and mixtures thereof, 65 to 80 weight percent of
said silane-treated microparticles and 10 to 25 weight
percent of pyrogenic submicron silica particles are mixed
with said polymerizable resin, and said composite has a net
surface area of 7 to 15 m^2/g, a compressive strength of at
least 440 MPa, and a diametral tensile strength of at least
90 MPa.

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